METHOD TO PREVENT RUSTING AND GENERAL OXIDATION FOR METALS AND NONMETALS

FIELD OF THE INVENTION

The invention relates to the general field of novel, cost-effective antirust and anti-oxidation measures to be applied on metallic and nonmetallic materials, or to be applied when making these materials, by employing long-life beta (electron) emitters. It is also with particular reference to the fields of creating new paints to suppress iron rusting; and of creating new alloys, including steels and cast irons, which are corrosion-preventive themselves. It is further referenced to the fields of creating novel packaging (with anti-microbial and anti-mold properties) and novel nonmetals, such as new ceramics (though containing both metallic and nonmetallic elements) and new biomaterials, that are resistant to undesirable oxidations rendered by various free radicals.

BACKGROUND OF THE INVENTION

Corrosion has been a major threat to quality and structural integrity of objects formed of either metals or nonmetals as time goes by, especially in adverse (or, corrosive) environments specific to each object. While manifesting itself through many forms under various circumstances, the physical cause of corrosion is essentially oxidation in the general sense. For example, iron bridges near coastline and oil drilling platforms above sea level rust (i.e., oxidized mainly by

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hydroxyl ions (OH$^-$) to form rust: $Fe(OH)_2$ and $Fe(OH)_3$) easily in the wet, salty (electrochemically corrosive) environment even under the protection of antirust paints. Similarly, naval vessels, commercial freighters, oil tankers, and ferries all corrode in time, while each having been anti-rust treated. Things surrounding our daily life rust, for example: cars, hammers, plows, refrigerators, underground cast iron conduits (oxidized by OH$^-$ ions, microbes, etc.), and even artificial implants within patients' bodies (oxidized largely by chlorine-related compounds). Situations are particularly worse when scratches remove their protective surface coatings, or pitted corrosions have occurred. For irons, it is a common practice to either electroplate it with other more-ready-to-oxidize metals (i.e., more active, such as zinc, to produce so-called galvanized iron) or manufacture it into alloys (such as the stainless steels) as means to prevent rusting. However, though being relatively costly approaches, the iron content rusts in the long run, i.e., as soon as the more active metals are consumed. Metals can also be oxidized by elements other than oxygen. For example, iron corrodes (or, electrochemically oxidized) in a sulfuric environment and eventually becomes rotten with iron sulfides.

Similar situation has been plaguing other important metals, for example, aluminum and copper, as well as their alloys. In fact, other than metals, even some nonmetals, such as ceramics

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(e.g., boron nitride, graphite), organic compounds, and polymers (such as rubber), gradually degrade after one or several of their molecular groups or metal components are oxidized by external oxidizing agents. For instance, exposure of polymers to oxygen, usually at elevated temperatures, alters the polymerized structure. In rubber, for example, oxygen provides additional cross-linking, causing the rubber to become harder or fatigue (see, Ege, Seyhan, Organic Chemistry 4th ed., pp. 1057-1058, Houghton Mifflin Co., New York, 1999). The condition can be much worse when in the high temperature environment. All the same, other nonmetals like biomaterials in general, including bio-products (such as foods) and living bio-systems, also suffer from undesirable oxidizations caused by environmental free radicals, and degrade seriously in quality. For example, cereals, cookies, rice products, dairy foods, etc. are spoiled and become rancid (actually toxic) when the double bonds of oil in them are gradually attacked by oxygen in the air. In fact, a gigantic amount of antioxidant additives, such as BHA and BHT are routinely applied in the world's food products, though health-wise undesirably. In the above, BHA stands for butylated hydroxyanisole, and BHT stands for butylated hydroxytoluene, or 2,6-di-tert-butyl-4-methylphenol (see, e.g., Ege, Seyhan, Organic Chemistry 4th ed., pp. 829, Houghton Mifflin Co., New York, 1999).

In spite of being a tough problem to tackle both technically and economically, the general notion of oxidative corrosion itself is fundamentally but a simple one. Namely, any oxidation reaction is involved with the robbing of electrons. Fig. 1 explains the inner working of oxidative corrosion in terms of the electrochemical cells (see, e.g., Lawrence H. Van Vlack, Elements of Materials Science and Engineering, Section 13-5, Addison-Wesley, Reading, MA, USA, 1985). On the anode1 side the surface deterioration of concerned material occurs by its component metal, M, losing electrons and becoming a positive ion (oxidative corrosion reaction):

$$M^0 \rightarrow M^{m+} + m\ e^-$$
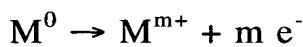
(1)

For the reaction to proceed, both the electrons and the metal ions must be removed from the anode 1, otherwise, the reverse reaction becomes significant and equilibrium is established. Note that the cathode 2 is usually made of a less active metal, namely metal with lower capability of releasing electrons, compared with the anodic metal M. The reaction taking place at cathode can be symbolized by $X + n\ e^- \rightarrow X^{n-}$, where X can be atom or ion from anode or environment. Namely, the electrons, flowing over to cathode 2 via metal connection 19, are accepted either by a nonmetallic element, N, or by the displaced metallic ions, M^{m+} on the cathode 2 side

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(thus, the cathode consumes electrons in a corrosion process):

$$N^0 + n \ e^- \rightarrow N^{n-}$$

(2)

Or, $\quad M^{m+} + m \ e^- \rightarrow M^0$
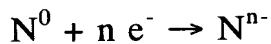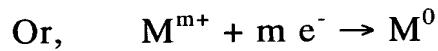
(3)

The metal ions of equation (1) either dissolve in the surrounding environment (e.g., liquid electrolyte) or combine with nonmetallic ions, to form a surface deposit on the cathode side. Hence, overall, the anodic metal M corrodes as a result of such electrochemical oxidation reaction. A good example is the corrosion of iron under a droplet of water or any deposit. Namely, one type of electrochemical cell, called concentration cell, develops when there is difference in the environments surrounding the anode and the cathode, respectively.

As depicted in Fig. 2, deposit 3, such as rust, microbes or water droplets shield the underlying metal (e.g., iron 17)) from oxygen (called oxygen starvation). Consequently, this low-oxygen region 4 undergoes anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$ and the metal corrodes, forming rust 18 at the boundary of the deposit 3 in the cathodic high-oxygen region 5, where the associated reactions are: $O_2 + 2 \ H_2O + 4 \ e^- \rightarrow 4 \ OH^-$ and $Fe^{2+} + 2 \ OH^- \rightarrow Fe(OH)_2$ (see, Donald R. Askeland, The Science and Engineering of Materials, pp. 792, PWS-KENT Publishing, Boston, MA, 1989).

Based upon the knowledge derived from the theory of

electrochemical cells, various anti-corrosion measures have emerged. One of them is the galvanic (or cathodic) protection, which is achieved by arranging for the product intended for protection to be the cathode. This in turn is realized via either the galvanic cell or the impressive voltage approach.

For the former, when two dissimilar metals are put together in contact, under an environmental condition, a particular electrochemical cell termed galvanic cell is formed. In it, the metal higher in the electromotive series as listed in Table 1 acts as the anode, while the other as cathode. For example, on a sheet of galvanized steel, the zinc coating acts as an anode and protects the underlying iron even if the surface is not completely covered (e.g., due to a scratch), because the exposed iron is the cathode and does not corrode. However, on the exposed iron surface, the aforementioned concentration cell can still develop once there is deposit, such as a water droplet, and the undesirable rusting will start (see, Fig. 2). Besides, as soon as the sacrificial metal is fully consumed, the cathodic protection it provides is lost and thus constant replacement of the sacrificial anode is required.

Similarly, stainless steels are stainless because their surfaces are passivated by the more anodic chromium (Cr), which forms oxide film when in contact with oxygen. However, if the service conditions are reducing and no oxygen is present, this passive layer can be destroyed. Without such protection,

the steel becomes active and the corrosion of Cr-bearing steels proceeds rapidly (see, Lawrence H. Van Vlack, Elements of Materials Science and Engineering, pp. 539, Addison-Wesley, Reading, MA, USA, 1985). In fact, for this reason many improving efforts are being spent on steels, as well as other metals using passivated layers. For example, Cueman et al. (US Patent 5,000,979, March 19, 1991) propose process for coating a metallic substrate for isolation from hostile environments.

Table 1. The electromotive force (emf) series for selected elements*

	Metal and nonmetal
Anodic	$Li \rightarrow Li^+ + e^-$
	$K \rightarrow K^+ + e^-$
	$Na \rightarrow Na^+ + e^-$
	$Mg \rightarrow Mg^+ + e^-$
	$Al \rightarrow Al^{3+} + 3e^-$
	$Ti \rightarrow Ti^{2+} + 2e^-$
	$Mn \rightarrow Mn^{2+} + 2e^-$
	$Zn \rightarrow Zn^{2+} + 2e^-$
	$Cr \rightarrow Cr^{2+} + 2e^-$
	$Fe \rightarrow Fe^{2+} + 2e^-$
	$Ni \rightarrow Ni^{2+} + 2e^-$
	$Sn \rightarrow Sn^{2+} + 2e^-$
	$Pb \rightarrow Pb^{2+} + 2e^-$

	$H_2 \rightarrow 2H^+ + 2e^-$
	$Cu \rightarrow Cu^{2+} + 2e^-$
	$4(OH^-) \rightarrow O_2 + 2H_2O + 4e^-$
	$Fe^{2+} \rightarrow Fe^{3+} + e^-$
	$Ag \rightarrow Ag^+ + e^-$
	$Pt \rightarrow Pt^{4+} + 4e^-$
	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Cathodic	$Au \rightarrow Au^{3+} + 3e^-$
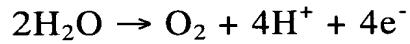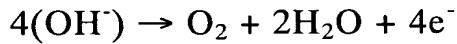
* Under the condition of 25°C, 1 atm and 1 M ion concentration. If the ion concentration is other than 1 M, then Nernst equation (see, ibid) has to be used to come up with the new ordering.

In the impressed voltage approach, a small DC voltage (such as drawn from an ordinary 3-5 V battery) keeps the protection-intended product negative in potential (thus cathodic) with respect to a reference ground in its environment. This effectively prevents rusting for many situations including equipments buried underground (e.g., piping system for natural gas) and automobiles. Further, some initial rust-attacked regions can be recovered by the supply of such negative electron current. However, there are several drawbacks. First of all, even though the needed anodic current is tiny, to maintain this kind of cathodic protection, regular replacement or maintenance of power source will be required. This becomes a significant setback when the environment is

highly corrosive and large electron current is continually consumed. Secondly, a physical anode will be needed, which itself will corrode and need replacement. Besides, the protected area is limited unless an anode large in size is employed. Thirdly, such anode emits so-called stray current causing undesirable interference with, and aggravated corrosion, on other nearby equipments. In other words, the DC current from the active anode creates unwanted new secondary anodes on its stray path prior to reaching the cathode (product under cathodic protection). Lastly, erroneous connection of DC polarity has been a common practical event, which has led to serious corrosions on protection-intended equipments.

Recently, a new "passive" impressive voltage method was proposed and demonstrated by utilizing the solar-generated voltage from a titanium oxide (TiO_2) solar panel (Park H. et al., J. Phys. Chem. B, 106, 4775-4781, 2002). Fig. 3 shows one of its proposed applications, in which an underground steel structure 9 is protected by a TiO_2 photoanode 6 above ground (covered under ITO glass16 and with holes constantly removed by the holes scavenger 7). Though still needing battery power 8 during nighttime, this approach eases the requirement of regular power source maintenance or replacement considerably.

However, it is noticed that a relatively large electron current (of the order of 10 μA) is continuously needed to

sustain the required impressed voltage. This is because, when without solar UV action, an electrochemical cell of anodic Fe vs. cathodic TiO_2 is formed and iron rusts (note: it is not a Ti-Fe cell as Table 1 might have suggested). In order to reverse the corrosive anodic reaction, i.e., making Fe cathodic instead, a relatively large electron flow from TiO_2, rendered by UV light, is needed (see, ibid). It is obvious, therefore, that to achieve the required impressive voltages on larger products would simply mean the need of larger solar panels. As a result, both the economic concern and problems related to ease of practical application will arise. What's more, as reminded of while presenting equation (1), holes scavenger 7 will be needed for the solar cathodic protection reaction to proceed. To this end, the effectiveness of this "passive" anti-corrosion method will be varying owing to the changing metal ion concentration within the holes scavenger. This inevitably adds further complications to its practical applications, making it unsuitable for situations needing versatility. Further still, as were true of all other existing cathodic protection schemes, other than the aforementioned application drawbacks, it does not save itself from the threat of concentration cells, which develop so long as there is non-uniformity of deposit coverage on the product and initiate the corrosion process.

Looking retrospectively in the human history, lots of resources and brains have been directed towards such

businesses as anti-oxidation and anti-rust measures including using of paints, alloys and additives for organic compounds and foods of various recipes, not to mention numerous coating, manufacturing and applying processes. However, up to this point the outcome has been a bit far from satisfactory.

SUMMARY OF THE INVENTION

It has been an object of the present invention to provide a passive and versatile method to robustly achieve anti-corrosion purposes on a wide-range of materials and situations for very long time.

A second object of the invention has been to provide a cost-effective, general anti-oxidation, and even reductive, method to be easily applied on metals and nonmetals.

A third object of the invention has been to provide a passive and robust anti-rust method that can either be applied directly on finished products, including creating novel anti-microbial and anti-mold packaging for them, or be applied when making these products.

A fourth object of the invention has been to provide a method to render oxidation-resistive capability for organic compounds, bio-products, such as food, and bio-systems, against oxidizing free radicals, bacteria and microbes.

Yet another object of the invention has been to provide a new impressive voltage anti-corrosion method, which does not require power source, anode, holes scavenger and metal

connection between the anode and the cathode.

The last object of the invention has been to provide a new cathodic protection method, which does not cause stray current corrosion on other equipments nearby.

These objects are fulfilled by providing a novel cathodic protection method in which the impressive voltage to render the product negative in potential (hence cathodic) is maintained by long-life beta emitters, such as Ni-63, instead of an external power source. As an isotope of Ni (nickel), Ni-63 is a pure beta emitter of a half-life of about 100 years, where the half-life is the time period for a fixed amount of radioisotope to decay to half of its original radioactivity. From the galvanic cell point of view, the beta emitter now serves the function of the new sacrificial anode with higher activity (or, capability of releasing electrons) than lithium in Table 1, and hence no physical anode is needed as in traditional impressive voltage approaches. In fact, the emitted beta particles (i.e., electrons) from Ni-63, each carrying an average of about 66 keV energy, are flying over, instead of simply flowing, to the product intended for protection. Thus, the required impressive voltage for cathodic protection can be passively achieved by the invented method using a fairly small amount of beta emitters (see, calculation in Embodiment 1). The beta decay process of nickel-63 is described by:

$$_{28}Ni^{63} \rightarrow {}_{29}Cu^{63} + e^-$$
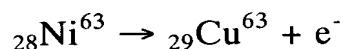
(4)

where the product copper-63 is a stable nucleus which undergoes no further decays.

Besides, in existing zinc (anode)-iron (cathode) protective coating schemes (i.e., employing ordinary anodic metals in Table 1), the amount of zinc ions (Zn^{2+}) reaches an equilibrium value to maintain a negative potential on the underlying iron. This equilibrium state is significantly altered when there is a scratch exposing the iron, and particularly so when there are salty water deposits and subsequently concentration cells develop. Namely, in the latter case, the protective $Zn \rightarrow Zn^{2+} + 2e^-$ reaction surrounding the scratch simply cannot be efficient enough in compromising the $Fe \rightarrow Fe^{2+} + 2e^-$ reaction, since the natural holes scavengers here are mere air and static paint on top of the zinc coating, and the exposed iron rusts rapidly anyway. In comparison, no holes scavenger is needed for the invented method, since as Ni-63 decays (via beta emission) spontaneously and efficiently into the stable neutral Cu-63 (see, equation (4)), no positive charges are left behind. Furthermore, formation of concentration cells as depicted in Fig. 2 can be effectively avoided, since the anodic reaction $Fe \rightarrow Fe^{2+} + 2e^-$ in the oxygen starvation region 40 (see, Fig. 4) will now be impeded and reversed, i.e., becoming $Fe \leftarrow Fe^{2+} + 2e^-$, by the abundant supply of electrons from beta emitters embedding in paint over iron surface or within iron 20 itself

(see also deposit 10, iron 20 and oxygen-rich region 60 of Fig. 4). To this end, the invented method is a much more effective measure in reducing the initial-phase rust back into iron by reverting the anodic reaction, than existing cathodic protection schemes.

To achieve the anti-microbial and anti-mold purposes, other than directly acting against the oxidizing effect imposed by the microorganisms, the invented method can also play the anti-metabolite role on the microorganisms themselves. It is now well-known that higher animals and microorganisms share a large proportion of internal biochemical mechanisms in maintaining their lives, for example, the biosynthesis of essential organic compounds, such as amino acids and vitamins, and in oxidation-reduction sequences on various compounds for nourishment (see, e.g., Solomons, T. W. Graham, Fundamentals of Organic Chemistry, 5th Ed., pp. 878-881, John-Wiley & Sons, New York, 1997). The passive anti-oxidative character of the invented method, with beta emitter such as Ni-63 incorporated in paint, \, alloys, etc., can naturally impede the vital oxidation reactions within these bacteria or microorganisms, and eventually expel these microscopic life forms from products intended for protection.

There are several long-life beta emitters that can be adopted by the current invention. They are, other than Ni-63 (nickel, half-life 100 years, 66 keV beta), for example, Cd-113

(cadmium, half-life 13.7 years, 590 keV beta) and Tc-99 (technetium, half-life 2.13×10^5 years, 293 keV beta) (see, e.g., Chart of Nuclides, General Electric Company, 1984). Ni-63 can be readily produced via the $_{28}Ni^{62}(n, \gamma)_{28}Ni^{63}$ reaction, by bombarding the stable Ni-62 isotope (natural abundance: 3.59 %, thermal neutron absorption cross-section: 14.5 barn; 1 barn = 10^{-24} cm^2) with thermal neutrons from a research type nuclear reactor, for example. In the above nuclear reactions, the common notation A(a,b)B was used, in which the target nucleus "A" is bombarded by projectile (or radiation) "a" to become product nucleus "B" together with a released particle (or radiation) "b." In addition, "n" stands for thermal neutron (about 0.025 eV) and "γ" stands for gamma ray. Similarly, Cd-113 can be produced via the (n, γ) reaction on stable Cd-112 (natural abundance: 24.13 %, thermal neutron absorption cross-section: 2.2 barn). As for Tc-99, there are at least two ways to produce it by working on Mo-98 (molybdenum, natural abundance: 24.13 %, thermal neutron absorption cross-section: 0.132 barn). One is via the $_{42}Mo^{98}(p, \gamma)_{43}Tc^{99}$ reaction, with p standing for proton (hydrogen ion); the other is through $_{42}Mo^{98}(n, \gamma)_{42}Mo^{99}$, and then a decay of a half-life of about 66 hours to Tc-99.

The beta particles (i.e., electrons), emitted by Ni-63 and carrying energy of about 66 keV, will pose no radiation threat to human beings, since electrons around that energy are too

weak to penetrate even the outermost layer of normal human skin. In addition, in the teaching of the current invention, since these beta emitters become an integral part of the substance, e.g., a paint (to be applied on products), a package, biomaterial, an alloy (e.g., eutectic welder), a ceramic, or a polymer, these electrons are further slowed down and stopped by atoms and molecules within that substance. Particularly, it requires only a very small amount of Ni-63 to accomplish the invented novel impressive voltage cathodic protection (see, calculation in Embodiment 1). Should there be occasions in which larger volume incorporation of Ni-63 is favored, they mostly will be related to crucially corrosive situations at remote sites where the concern over noticeable harm to humans normally will not materialize. In fact, in these situations, even beta emitters of higher energy can be properly employed.

Production and application of radioisotopes, including beta emitters, should follow the safety guidelines set by the Nuclear Regulatory Commission (NRC) in the US and International Atomic Energy Agency (IAEA) in the world. Normally, the threshold amount of Ni-63 requiring a regulatory license for operation is around 5×10^4 Bq ($= 1.35$ μCi, 1 Ci $= 3.7 \times 10^{10}$ disintegration/s (or Bq, i.e., Becquerel)). In other words, for a product, or an ensemble of products, containing less than this threshold level of Ni-63 radioactivity can be freely processed or maneuvered if documented and

reported. It will be shown in the following preferred embodiments that nuclear regulatory guidelines can be readily complied in realizing the current invention (see, Embodiment 1).

Note that although there already are a huge pile of prior arts concerning incorporation of radioisotopes, including numerous ways of coating, alloying them onto other substrates for different purposes, none of these prior arts show relevance to the important issue of isotope-rendered anti-rust (or, general anti-oxidation) measures as described by this invention. This observation can be readily proven after one is acquainted with the status quo of existing anti-rust practices. However, this is not surprising, as normally radioisotopes are considered hazardous when applied within our daily environment. Owing to this perception, long-life (on the order of 100 years, so of small decay constant), low-energy (much less than the MeV level) beta emitters, such as the adopted nickel-63, have so far been overlooked for such novel and safe applications.

Among existing prior arts involving radioactive coating, only one is associated with anti-oxidation, though still not rendered by radioisotopes. Yokoyama and Hanioka (European Patent EP 0338838, Oct. 25, 1989) teach freshness preservative packing material for foodstuffs and method of fixing the freshness preservative substance onto the packing material. The freshness preservative material of theirs contains:

far-infrared (IR) "radioactive" substance of about 3 μm to14 μm wavelength (characteristic of ordinary thermal radiation), a gas adsorptive substance, and an oxygen reactive substance. Crushing and graining a solid substance emitting far-IR rays (or, heat), such as heat generating ceramics accordingly prepares the "radioactive" substance. By absorbing the far-IR rays freshness of vegetables, meat, and fish is claimed preserved. The gas adsorptive substance, on the other hand, getters the maturity-accelerating ethylene gas released by vegetables and fruit themselves. The oxygen reactive substance (e.g., iron, aluminum, copper, and ascorbic acid) takes up oxygen within foods. Apparently, the anti-oxidation role is not played by any direct action of radioactive isotopes.

Other more irrelevant prior arts are: Snow et al. (Patent PCT/US00/14389, May 24, 2000) teach method of coating a metal substrate with a radioactive layer mainly for the brachytherapy purpose, i.e., in which a radioactive source is put into the body of a patient to irradiate a diseased tissue in proximity.

Hampikian and Scott (Patent PCT/US99/19998, May 25, 2000) disclose radioactive coating solutions (or, sols, sol-gels) for general metal coatings on substrates, via mainly electro-deposition and electroless deposition. Each of their solutions comprises at least one dissolved carrier metal ion, and either an insoluble radioisotope or an insoluble compound

of a radioisotope suspended within the solution. Their concerned radioisotopes are like P-32 ($t_{1/2}$: 14.28 days), S-35 ($t_{1/2}$: 87.2 days), Y-90 ($t_{1/2}$: 64.0 hours), and Au-198 ($t_{1/2}$: 2.69 days), all being beta emitters of relatively short half-lives, where $t_{1/2}$ stands for half-life. Their applications include separation of isotopes, making radioactive medical devices, producing asymmetric radiation fields, and morphology of tumors. In comparison, aside from the novelty of the invented anti-rust method and also great difference in radioisotopes of interest, the beta emitter (say, nickel-63) itself, of the current invention, will be both the provider of negative charge carriers (i.e., emitted electrons) and the radioisotope, should electro-deposition or electroless deposition be adopted as the coating means (see also Embodiment 1 for many other means).

Similarly, Chan et al. (US Patent 2002/0143228, Oct. 3, 2002) teach radioactively coated devices, especially radioactively coated medical devices using mainly immersing, electro-deposition, and electroless deposition methods.

Ludger et al. (Germany Patent DE 10112518, Sept. 19, 2002) disclose a radioactive medical stent comprising coating of radioactive isotope for preventing restenosis of blood vessels.

Kling(US Patent 4,761,583, Aug. 2, 1988) teaches glow discharge starter containing radioactive alloy to reduce the undesirable dark effect at the starting of a glow discharge, by

lowering the work function needed to achieve a voltage breakdown.

Note that, although the current invention can provide fairly robust, lasting and versatile anti-oxidation solutions to potentially numerous circumstances, it never claims to be the most elegant or suitable sole solution to all situations we mankind have encountered or will encounter. In fact, this invention can achieve the most when all existing experiences and arts are paid due respect.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is the well-known electrochemical cell mechanism based on which the general corrosion theory is formed.

Fig.2 is the known process of development of concentration cell (a special case of the general electrochemical cell) as a result of deposit on the metal surface.

Fig.3 is one application of an existing "passive" anti-rust proposal in which a photoanode above ground maintains the required impressive voltage for cathodic protection of an underground iron structure.

Fig.4 is the way the invented method reverses and impedes the undesirable oxidative anodic reaction of a concentration cell on iron via supplying electrons from beta emitters such as Ni-63.

Fig.5 is an example of iron surface protection of this

invention using paints or coatings incorporated with very long-decay-life beta emitter Ni-63.

Fig.6 is an application of the invented method in producing beta-emitter-rendered anti-corrosion artificial bones (biomaterials).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

EMBODIMENT1 : Protection of cast irons and steels using paints or coatings containing beta emitters

Both cast irons and steels are essential materials widely used by many industries. However, they both are plagued by rusting seriously. For this reason, costs of anti-rust efforts spent on them alone have annually constituted significant percentages to GNPs worldwide, even though the problem remains untamed. In this embodiment, the invented method is realized by incorporating long-life beta emitters into paints or coatings before applying the latter on products made of cast irons and steels. That is, now, a novel passive and lasting (> 100 years) impressive voltage cathodic protection is established by letting these products carry a negative potential as a result of receiving emitted electrons from such paints or coatings. Fig. 5 depicts an example in which the iron structure 100 is protected by the nickel-63-carrying paint 80, as well as an optional extra coating 120 over the paint 80.It is to be noted that the electrons130 are all emitted from region 80.

The ease with supplying a needed negative potential by this invention can be demonstrated by the following calculation. Take an iron circular disk with a large radius R for example. If the surface charge density is denoted as σ (= Q/A, Q is total charge, A is area), then the potential variation along the central z-axis perpendicular to the disk plane (where z = 0) is (see, Haus, Herman A., Electromagnetic Fields and Energy, 5th Ed., pp. 104-105, Prentice Hall, NJ, 1989, in SI unit):

$$\Phi = \frac{\sigma}{2\varepsilon_0}\left(\sqrt{R^2 + z^2} - |z|\right)$$

(5)

where $\varepsilon_0 = 8.85 \times 10^{-12}$ Farad/meter is the permittivity of free space. The reference $\Phi = 0$ is, in theory, at an infinite distance from the iron disk (i.e., z $\rightarrow \infty$)(since as z>>R, $\Phi \approx \sigma R^2/(4\varepsilon_0|z|)$). However, for practical purposes, at a distance of z > 2R, for example, will suffice to justify Φ there as a practical reference (i.e., $\Phi \approx 0$) and Φ of equation (5) as an approximate value of the potential at z. If the total number of Ni-63 atoms initially applied on the iron surface is $N_A{}^0$, and Q = N·(-e) (when the draining of electrons into environment is negligible comparing with the loading of electrons during this initial phase), then N $\approx N_A{}^0$·(1-e$^{-\lambda t}$), where $\lambda = 2.2 \times 10^{-10}$ s^{-1} is the decay constant of Ni-63, e = 1.6 $\times 10^{-19}$ C is the single electron charge, and t stands for time elapsed since the application of the invented paint. Thus, from equation (5), for R >> z (i.e., near iron surface) we have:

$$\Phi \approx -\frac{N_A{}^0 \cdot e \cdot (1 - e^{-\lambda t})}{2\pi\varepsilon_0 R}$$

(6)

For R ≈ 1 m, and a tiny amount of Ni-63, e.g., $N_A{}^0$ ≈ 6.02 x 10^{13} (i.e., ten billionth of a mole, or around 0.006 μg of Ni-63), it takes only about 36 hours to reach −5 volt on the iron surface. Then, equilibrium will be established between the supply and draining of electrons, whose precise value is to be determined by the real circumstances. Such achieved cathodic protection will last for more than 100 years. The related maximum radioactivity is $\lambda N_A{}^0$, and is 1.3 x 10^4 Bq, which easily complies with all relevant nuclear regulatory rules. Nonetheless, in those special situations where the environments are highly corrosive (i.e., the draining current of electrons is significant), higher concentrations of beta emitters will be necessary and consequently stricter monitoring operations will have to be enforced.

Unlike existing schemes of cathodic protection, which all succumb to corrosions caused by the development of concentration cells (see, Fig. 2) owing to various external factors, the current invention will instead reverse the Fe → Fe^{2+} + 2e⁻ reaction by supplying abundant electrons from beta emission and thus suppress the formation of concentration cells, or more specifically, the creation of oxygen-starved anode (see, Fig. 4). Further, instead of causing stray-current-induced corrosions on nearby equipments as

relevant to traditional impressive voltage methods (which totally rely on employing anodes to form a closed electric circuit), the negative electrons emitted by beta emitters of this invention, on the contrary, will reach out to provide extra cathodic protection, originally absent, for these equipments. In other words, since there is no need for a closed electric circuit to realize this invention, these nearby equipments are merely put on negative potentials by the emitted straying electrons and thus would refrain from becoming anodes and corroding subsequently.

There are a number of ways to incorporate beta emitters into paints and coatings (including lacquers). For example, bombarding fine powders of nickel-62 with thermal neutrons drawn from a research type nuclear reactor can readily produce Ni-63-rich fine powders. Or, nickel-62 foils can be employed instead, to generate Ni-63-rich samples before being dissolved in nitric acid for subsequent application onto surfaces of iron or steel products. The nitric acid itself then evaporates in the end. There is extra benefit for the latter approach. Namely, when iron, e.g., is exposed to nitric acid, the iron rapidly and uniformly corrodes to form a thin, protective iron hydroxide coating and additionally achieves the so-called "anodic protection" (see, Donald R. Askeland, The Science and Engineering of Materials, pp. 797, PWS-KENT Publishing, Boston, MA, 1989). Note that in the

spirit of this embodiment, the invented method covers general painting and coating schemes already being routinely applied in various situations. They include, for example, brush painting, powder coating, thermal spray coating, diffusion coating, conversion coating, electro-deposition, electroless deposition, electroplating, anodizing, etc., and on automobiles, bridges, towers, tools and so on. In the cases where electro-deposition or electroless deposition be adopted as the coating means, the nickel-63 itself will be both the provider of negative charge carriers and the radioisotope, as compared to the disclosure of Hampikian and Scott (Patent PCT/US99/19998, May 25, 2000), whose solution comprises at least one dissolved carrier metal ion, and either an insoluble radioisotope or an insoluble compound of a radioisotope suspended within the solution.

EMBODIMENT 2 : Manufacturing of beta-emitter-included novel steels, alloys, ceramics, composites and polymers as new anti-corrosion materials

In this embodiment, the beta emitter, such as Ni-63, is incorporated as an integral part of the products during their manufacturing. The high temperature associated with, say, metal melting, will not cause damage to these beta emitters, since normal heat (i.e., not nuclear-reaction-causing) does not destroy the radioactivity of spontaneous nuclear decays. Hence, Ni-63-incorporated metals, alloys or compounds, such as

steels, composites, ceramics, and polymers can be readily generated. In this way, many new, lasting (e.g., more than 100 years) anti-corrosive materials, as well as their new applications, will emerge. For example, for metals, anti-rust eutectic in welding, anti-chlorine steels in concrete bridges, anti-halogen iron tanks in industrial chemicals production; and anti-oxidation rubber, anti-corrosion ceramic chambers, etc., for nonmetals.

EMBODIMENT 3 : Manufacturing of beta-emitter-included packaging for the food, medical and pharmaceutical industries

When organic compounds are exposed to air, they react slowly with oxygen to give hydroperoxides. This slow oxidation reaction is called autooxidation, and is responsible for the slow deterioration in air of foods, medicine, pharmaceuticals, and even paints. The reaction is further catalyzed by light, which is why these organic reagents are stored in cans or dark-colored bottles. Oxygen reacts to compounds containing double bonds, e.g., of polyunsaturated fatty acids in foods, by free-radical chain reactions (see, e.g., Ege, Seyhan, Organic Chemistry 4th ed., pp. 820-823 & pp. 829, Houghton Mifflin Co., New York, 1999). If these reactions are not stopped, the oils in food and medical products stored at room temperature in warehouses and on supermarket shelves are gradually oxidized and become rancid. Not only do rancid oils taste bad, they are also toxic. Additives

such as the aforementioned BHA and BHT are employed to break up the free-radical chain reactions by reacting themselves with any radicals that form. In other words, phenols in BHA and BHT lose electrons to free radicals. However, additives are usually undesirable concerning human health, especially they are known to be related to risk of carcinomas, according to many clinic reports.

This embodiment shows that the invented method can save the great cost of economy and risk of human health as a result of using such additives. Namely, proper Ni-63-included packaging can prevent the entering oxidizing radicals in air or environment from reacting with products. In other words, these low-energy electrons emitted from the package fulfill the electron-hungry needs of oxidants surrounding the products. This is to compare with the food preserving packing approach of Yokoyama and Hanioka (European Patent EP 0338838, Oct. 25, 1989) where the anti-oxidation role is played by oxygen reactive substances such as iron, aluminum, copper, and ascorbic acid.

The packaging materials containing Ni-63 can use paper tissue, polymer (including plastics, rubber), glass, metal foil, and so on, and can be in the form of packing box, bag, wrapping paper, etc. The required proper amount of Ni-63 can be determined according to each specific condition, and incorporated by methods such as spraying, printing, painting

and coating. Usually it will be on the low radioactivity side, since the concerned oxidation reactions are mostly slow ones.

EMBODIMENT 4 : Production of new anti-corrosion biomaterials for use with human body

Implanting devices into human bodies has been a common practice these days, including surgical implant of artificial bones, rehabilitation and cosmetology materials, denture, cardiac pacemaker, orifice, etc. These implanted biomedical materials need to be of very low corrosive rates in the bodily fluid containing high content of chlorides, and the corrosion-induced formations should not cause toxicity and harm to body tissues, such as pain, blood coagulation, infection, interference to tissue growth or bodily reactions. In addition, there are wide-ranged medical considerations. For example, in some occasions, porously sintered metals are preferred in regards to rendering better growth of bones and muscles. Further, the somewhat rust-resistive stainless steels may not be suitable for many occasions as they contain nickel, which causes allergies to some patients especially when the steel starts to corrode. As a result of such medical complexity and high standards, it is often hard to select biomaterials for different purposes under varying conditions in terms of their suitability and economy. The current invention offers alternative options by providing anti-corrosion capability to those low-cost and yet bodily-compatible biomedical materials

for different situations.

For example, in the high chloride bodily environment, Co-Cr or Ti (titanium) alloys in general are more sustainable than stainless steels, even though they too corrode, especially when in contact with other metals (leading to galvanic, pit and crevice corrosions). In addition, they are much more expensive and may not be favored from the bulk mechanic property perspectives. An alternative provided by the invented method might be a Ni-63-containing steel structure enveloped by a Co-Cr coating. The electrons emitted by Ni-63 can prevent both the steel and the Co-Cr coating from being oxidized and corroded. Besides, bodily tissue will not be exposed to nickel within steel and rendered allergic effects (see, Fig. 6 for an application of the invented method: a nickel-63-carrying artificial steel leg 140 is coated with Co-Cr alloy 160). Similar approaches can be taken on other alloys, composites, polymers and ceramics where appropriate.

EMBODIMENT 5 : Creation of anti-metabolites on microbes adhering to ship hulls, bridges, oil-drilling platforms, condensers and underground equipments

Microbial corrosion and thus-induced further deterioration have been a serious threat to equipments in soil, inner wall of conduits, heat exchangers, condensers, oil tanks of aircrafts, oil-drilling platforms and ship hulls. It is known that many kinds of bacteria, algae, fungi, mold and mildew have been

contributing to these phenomena via feeding on water and organic substances surrounding them. Almost all microbial organisms will establish oxygen concentration cells using their micro-organic membranes or secreted adhesives as deposits. Some better-known ones are (see, e.g., Bradford, Samuel A., Corrosion Control, Chapman & Hall, 1992), firstly, sulfate-reducing bacteria (SRB), which reduce sulfate ions (SO_4^{2-}) in soil to sulfide ions (S^{2-}), the latter further combining with ferrous ions (Fe^{2+}) from oxygen-starvation regions of iron (as the anode) to form iron sulfides (FeS). These precipitates of iron sulfides then serve as more efficient cathode than iron and accelerate the corrosion of iron in the oxygen-rich regions. Another acid-producing bacteria (APB) oxidize sulfur or sulfide to become sulfuric acid (H_2SO_4), which in turn serves as strong oxidant to many materials. The iron-oxidizing bacteria (IOB) feed on ferrous ion (Fe^{2+}) to produce ferric ions (Fe^{3+}), which in turn form rust clusters of haematites (Fe_2O_3). Additionally, microbes adhering to the bottom of ship hulls often attract further accumulation of other marine creatures feeding on them. This has always resulted in increased fuel spending for the ships.

Note that in all microbial corrosion processes, biochemical reactions within the microbial bodies are essential. For example, the corrosion conducted by a SRB is accomplished via the catalyst action of the enzyme for hydrogenation within

its body. Therefore, other than aiming at the corrosion processes themselves (here imposed by the microbes) as in all above embodiments, the current invention can also play the anti-metabolite role in expelling the microbes themselves. In other words, though constituting no threat to human beings, the invented anti-oxidation method can seriously hamper the vital biochemical oxidation-reduction sequences for life within these microorganisms and ultimately drive them away. For example, interfering with oxidation reactions belonging to the vital oxidative phosphorylation process (see, e.g., Dr. Michael W. King's biochemistry website http://web.indstate. edu/thcme/mwking/home.html) apparently will trigger sequential detrimental effects within these microorganisms.

Therefore, as revealed by this embodiment, the invented method can provide both the anti-oxidation and anti-microbial solutions. In particular, ship hulls and docks, either treated by Ni-63-containing paints or themselves made of Ni-63-containing alloys, are lastingly (> 100 years) resistive to rusting as well as marine creature adhesion at their bottoms.

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made without departing from the spirit and scope of the invention. For example, the employable beta emitters can also be other nuclides

characterized by half-lives less than 10 years for some shorter-term purposes. Beta emitters can be prepared in the organic compound forms, instead of in pure elements or elemental solutions.